

# PATENT SPECIFICATION

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DRAWINGS ATTACHED.

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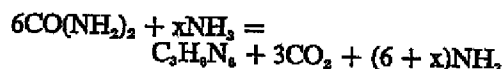
## COMPLETE SPECIFICATION.

### Process for the Production of Melamine.

We, NISSAN KAGAKU KOGYO KABUSHIKI KAISHA, a Corporation duly organized under the laws of Japan, of 2-2, 1-Chome, Nihonbashi-Honcho, Chuo-ku, Tokyo, Japan, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The invention relates to a process for the production of melamine, which consists of a carbon dioxide-ammonia system for producing urea and a urea-ammonia system for producing melamine, the waste gas obtained from the latter system as a by-product being utilized for the synthesis of urea in the former system and the urea produced in the former system being circulated to the latter system as a material for melamine synthesis.

The reaction formula for transforming urea into melamine in the presence of added ammonia is as follows:



From this reaction waste gas is obtained composed of carbon dioxide and ammonia.

In the above formula, the value of  $x$  is known to range from 42 (ammonia to urea by weight is about 2:1) to 0 but on the average the preferred value of  $x$  is approximately 10. Thereby the composition of waste gas by volume is 16% carbon dioxide and 84% ammonia. From the fact that this composition is nearly the same as the mol ratio used in the common process for urea synthesis, i.e. ammonia/carbon dioxide = from 3/1 to 5/1 it would be easy to infer that if this waste gas is employed to synthesize urea and the urea obtained is again used to synthesize melamine, the result will be production of melamine via urea from carbon di-

oxide and ammonia. However, the practical realization of the above process meets with the following difficulties:

(1) The pressure under which urea is synthesized is usually over 200 kg/cm<sup>2</sup> (this is absolute pressure). Meanwhile, the pressure of melamine waste gas is less than 200 kg/cm<sup>2</sup> and its temperature ranges from 360°C to 450°C. This means that if said waste gas is to be directly sent under pressure to the urea-synthesizing tower, the installation of a high-temperature, high-pressure gas pump, blower, compressor, etc. is necessary and this hinders the industrial use of the process. (2) Even if a melamine waste gas at more than 200 kg/cm<sup>2</sup> is obtained from the melamine-producing system, the hot melamine waste gas, directly sent into the urea-producing tower, will cause bubbles, occupying a part of the space in said tower, until it cools down to the appropriate liquid temperature for urea synthesis; thereby the reacting volume for the urea synthesis will drop, as the result lowering the efficiency per unit volume of urea synthesis. Moreover, around the inlet of the waste gas a local hot spot will be created. This is undesirable from the standpoint of mechanical strength and corrosion resistance of the device.

(3) When melamine and waste gas are separated under relatively low pressure (from atmospheric pressure to several times that pressure) and low temperature (below 250°C), only a low-concentrated aqueous solution of ammonium carbamate will be obtained and it will be necessary to increase the circulation of ammonium carbamate, thereby making it difficult to maintain the temperature in the urea-producing tower and lowering the conversion efficiency of said tower. Besides, the thermal energy of the hot waste gas will be wasted.

We have investigated the direct utiliza-

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tion of the melamine waste gas for the synthesis and have successfully solved the above-mentioned difficulties. A melamine waste gas of ammonia, and carbon dioxide, which is discharged from the top of the melamine reaction vessel is introduced directly without any treatment into the waste gas absorption cell operated at 130–160°C and 60–150 kg/cm<sup>2</sup> in the recycle circuit of aqueous ammonium carbamate to the urea synthesis.

Thus, the said waste gas is utilized as a concentrated aqueous solution of ammonium carbamate for the urea synthesis; on the other hand the sensible heat of said waste gas and the heat released in the formation of carbamate are exploited for decomposition of unreacted ammonium carbamate in the urea-synthesizing liquid and for generation of steam, and, further excessive ammonia is refined and recovered as liquid ammonia in the waste gas absorption cell.

In this invention the process of transforming urea into melamine is made to occur under a pressure of 60–150 kg/cm<sup>2</sup>, the operating conditions of the waste gas absorption cell, i.e. the temperature 130–160°C and the pressure 60–150 kg/cm<sup>2</sup> have been selected to assure perfect absorption of melamine waste gas by the aqueous solution of ammonium carbamate and for effective heat recovery. If the temperature is higher than this selected value, perfect absorption of melamine waste gas will be hindered; on the other hand, if the temperature is lower than that, the heat recovery efficiency will drop. The operating pressure depends on the temperature; namely, low temperature corresponds to low pressure, while high temperature corresponds to high pressure.

The present invention is applicable to what is commonly called the aqueous solution circulating method of urea synthesis. Detailed features are as follows:

(a) The pressure in the waste gas absorption cell is equal to that in the melamine reaction vessel, so that the melamine waste gas can be introduced without raising its pressure directly into the waste gas absorption cell. Thus there is no need for any special installation to carry the high-temperature high-pressure gas, which is a great help to the industry.

(b) Since the melamine waste gas is introduced into the urea-producing tower after it has been fully absorbed as an aqueous solution of ammonium carbamate in the waste gas absorption cell, there is no possibility of bubble generation or local heating in said tower.

(c) The melamine waste gas with a temperature of 360–450°C and a pressure of over 60 kg/cm<sup>2</sup> is recovered as a concentrated aqueous solution of ammonium car-

bamate in the waste gas absorption cell of the recycle circuit and is used in the urea-producing system and any new addition of water is rendered unnecessary. Thus, the temperature in the urea-producing tower can be maintained and the conversion efficiency of said tower can be enhanced.

(d) As the operating temperature of the waste gas absorption cell is 130–160°C, the sensible heat of melamine waste gas and the heat of ammonium carbamate formation can be utilized for decomposition of unreacted ammonium carbamate and generation of steam.

(e) When the amount of ammonia in the waste gas absorption cell becomes excessive the excess ammonia can be recovered as liquid ammonia through high pressure distillation from the top of waste gas absorption cell; and this ammonia can be reused in the melamine synthesis.

To explain the invention further reference is made to the attached drawing which is a flow sheet illustrating the process of the invention. A fresh supply of ammonia to the melamine-producing system goes through a pipe 1 and is compressed by a pump 2.

Meanwhile, the ammonia recovered in the waste gas absorption cell 35 goes through pipe 7 and is compressed by pump 8. Both ammonia gases pass through a preheater 3 and reach the bottom of the melamine reaction vessel 4.

On the other hand, the molten urea goes from the urea-producing system via pipe 5 to pump 6, where it is compressed; and then it is introduced through pipe 9 into the melamine reaction vessel 4.

The melamine reaction vessel 4 is divided by a partition board 11 into upper and lower reaction zones. In the first stage reaction zone at the upper part, the greater part of the reaction from urea to melamine takes place and the reaction product goes down descending pipe 12 into the second stage reaction zone at the lower part, where the transformation of said product into melamine is completed. The first stage reaction zone has a large number of electric heaters 10 arranged from the top of said reaction vessel 4.

The melamine reaction vessel 4 is kept at 360–450°C and 60–150 kg/cm<sup>2</sup>; and the purity of melamine obtained is more than 99%. The melamine obtained goes through an extraction tube 14 and is discharged out of an extraction valve 15. Said valve 15 is so interlocked with a liquid level indicator 13 that the liquid level of the first stage reaction zone may be controlled. The molten melamine flowing out of said valve 15 is sent to a high pressure cooler 16 which is maintained at 20–70 kg/cm<sup>2</sup> and there the melamine is cooled by the vapourizing liquid ammonia which is sent in from pump 26.

The solidified melamine dissolves in the mother liquor which comes from the pump 24 via pipe 23, thus melamine solution is yielded.

Said melamine solution goes through pipe 17 to valve 18, where it is depressurized to atmospheric pressure; then it is introduced into a melamine slurry tank 19. The greater part of the liquid ammonia which has been supplied to the high pressure cooler 16 is recovered at the slurry tank 19 and transformed into liquid ammonia by an ammonia condenser 25, to be recirculated to the high pressure cooler 16. The melamine slurry which has been separated from ammonia at the slurry tank goes through a crystallizer 20 and a centrifuge 21 and is yielded as the end product 22.

In the meantime, the melamine waste gas, i.e. a by-product of the melamine reaction, which consists of ammonia and carbon dioxide, passes pipe 40 and goes to the bottom of the waste gas absorption cell 35 which contain the heat-recovery coil 34 and steam recovery coil 36 and is kept at 130—160°C and 60—150 kg/cm<sup>2</sup>.

The sensible heat of the melamine waste gas, and the reaction heat generated through ammonium carbamate formation from waste gas in the aqueous solution of ammonium carbamate sent in via pump 55 and pipe 56 from the first condenser 54, are taken up in the heat recovery coil 34 for decomposition of unreacted ammonium carbamate in the urea-producing system and in the steam recovery coil 36 for generation of steam.

At the top of the waste gas absorption cell 35 (which contains the coils 34 and 36) installed an ammonia refining tower 37 which recovers ammonia in the form of liquid ammonia and recirculates it as material for melamine production, as described above.

The concentrated aqueous solution of ammonium carbamate formed in the waste gas absorption cell 35 goes through pipe 38 and pump 39 and reaches the urea-producing tower 31. On the other hand a fresh supply of ammonia through pump 28 and pipe 27, and carbon dioxide through compressor 30 and pipe 29, respectively also go to the urea-producing tower 31. Said tower 31 is kept at a temperature of 180—200°C and a pressure of 180—220 kg/cm<sup>2</sup>; and the urea-producing liquid obtained is depressurized by the valve 32 to 40—60 kg/cm<sup>2</sup> and goes to the heat recovery coil 34 via pipe 33. The unreacted ammonium carbamate and excess ammonia in said liquid are partially decomposed through depressurizing, further decomposed at the heat recovery coil 34, and in a mixed liquid/gas phase goes via pipe 41 to the first separator 42, where gas and liquid are separated. Thereupon the decomposed gas consisting of ammonia, carbon dioxide and water vapour goes via pipe 53 into the

first condenser 54, where it is absorbed in a dilute aqueous solution of ammonium carbamate which has been sent in from the second condenser 50 via pump 51 and pipe 52. The resulting aqueous solution of ammonium carbamate has its pressure raised at pump 55 and then via pipe 56 flows into the waste gas absorption cell 35. Meanwhile the urea liquid taken out of the bottom of the first separator 42 still contains a part of the unreacted ammonium carbamate and it is depressurized by valve 43 to 2—5 kg/cm<sup>2</sup>; then it passes through heater 44 into the second separator 45. The heater 44 further decomposes unreacted ammonium carbamate, while the second separator 45 separates gas from liquid. The separated mixture of ammonia, carbon dioxide and water vapour goes through pipe 49 into the second condenser 50, where said mixed gas is condensed, liquified and then recirculated via the first condenser 54 and the waste gas absorption cell 35 to the urea-producing tower 31. The urea liquid taken out of the second separator 45 via pipe 46 contains some water and a little ammonia and carbon dioxide. This liquid is sent to the concentrator 47 and the resulting liquid is recirculated for use in the melamine-producing system. When the production of urea exceeds the necessary quantities for melamine production, excess urea may be taken out of the system as end product 48.

A specific example of this invention is given below:

#### EXAMPLE

3,020 kg/hr urea and 1,590 kg/hr ammonia were used for producing 1,000 kg/hr melamine. In this process a waste gas of 2,446 kg/hr ammonia and 1,108 kg/hr carbon dioxide was obtained at 400°C and 100 kg/cm<sup>2</sup>. Said waste gas was introduced into the bottom of a stainless steel-lined waste gas absorption cell with 1 m inner diameter and 8 m height and there it was absorbed in a recycle aqueous solution of ammonium carbamate.

Said aqueous solution of ammonium carbamate, containing by weight 45.0% ammonia, 31.8% carbon dioxide and 23.1% water, was fed into the upper part of the waste gas absorption cell at a rate of 8,242 kg/hr at a temperature of 120°C. Said waste gas absorption cell was operated at 158°C and 90 kg/cm<sup>2</sup>. The urea-producing liquid flowed through the coiled pipe internally installed at a rate of 12,760 kg/hr. The sensible heat of melamine waste gas and the heat of ammonium carbamate formation were utilized for decomposition of unreacted ammonium carbamate (2,240 kg/hr ammonia, 1,580 kg/hr carbon dioxide, 375 kg/hr water) and for generation of 1,100 kg/hr steam at 4 kg/cm<sup>2</sup>.

466 kg/hr liquid ammonia was recovered at the top of the high pressure refining tower, 600 mm in diameter and 6 m high, which was installed on the top of the waste gas absorption cell. Meanwhile, aqueous solution of carbamate containing by weight 50.3% ammonia, 33.0% carbon dioxide and 16.7% water was obtained at a rate of 11,330 kg/hr at the bottom of said cell and was pumped to the urea-producing tower.

When this aqueous solution of ammonium carbamate and a new supply of 1,430 kg/hr carbon dioxide were used, the ammonia excess in the urea-producing tower amounted to 43% by weight. Then after reaction at 185°C and 200 kg/cm<sup>2</sup>, a mixture containing by weight 25.4% urea, 30.3% ammonia, 21.8% carbon dioxide and 22.5% water was obtained at a rate of 12,760 kg/hr. Thus, 92.8% by weight of ammonia absorbed from melamine waste gas could be converted to urea.

Further, when the addition of ammonia was insufficient in the reaction from urea to melamine or when large quantities of urea were to be produced for other purposes than melamine production, new supplies of ammonia and carbon dioxide were sent to the urea-producing tower, together with the aqueous solution of carbamate.

#### WHAT WE CLAIM IS:—

1. A process for the synthesis of melamine which consists of an aqueous carbon dioxide-ammonia system for producing urea operating at 180–200°C and 180–220 kg/cm<sup>2</sup>, the product being depressurized to

40–60 kg/cm<sup>2</sup>, and a urea-ammonia system for producing melamine operating at 360–450°C and 60–150 kg/cm<sup>2</sup>, the melamine waste gas, a by-product of the latter system being utilized for urea synthesis in the former system and the urea obtained from the former system being circulated to the latter system as material for melamine synthesis wherein the waste gas from the melamine comprising ammonia and carbon dioxide which is discharged from the top of the melamine reaction vessel is introduced directly without any treatment into a waste gas absorption cell which is operated at 130–160°C and 60–150 kg/cm<sup>2</sup> in the recycle circuit of aqueous ammonium carbamate in the urea-producing system, the resulting concentrated aqueous solution of ammonium carbamate being used for urea synthesis in the urea producing system; the sensible heat of the said waste gas and the heat of ammonium carbamate formation being utilized for decomposition of unreacted ammonium carbamate and generation of steam; and the excess ammonia being recovered as liquid ammonia in the waste gas absorption cell.

2. A process for the synthesis of melamine substantially as herein described with reference to the Example.

3. Melamine produced by the process of either of the preceding claims.

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COMPLETE SPECIFICATION

1 SHEET

This drawing is a reproduction of  
the Original on a reduced scale

